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COMPARISON OF METHODS OF EVALUATING CORROSION QUALITIES OF OILS IN THE DK-2 and PZZ INSTRUMENTS

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COMPARISON OF METHODS OF EVALUATING CORROSION QUALITIES OF OILS IN THE DK-2 and PZZ INSTRUMENTS

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The anticorrosion quality of oils is one of its most important operational qualities because it determines to a considerable degree the corrosion and wear of engine parts. The corrosion qualities of oils are usually evaluated by the unit losses of the weight of the lead plates (grams per square meter) when the oil is oxidized in the Pinkevich instrument (GOST 5162-49), the DK-2 instrument NAMI /Central Scientific Research Institute of Automobiles and Automobile Engines/ (GOST 8245-56) or the PZZ instrument (GOST 13300-67). To compare the most widely used methods of evaluating the corrosion qualities of oils, the NIIAT /State Scientific Research Institute of Automotive Transportation/ made laboratory tests on a number of oils with and without additives on the DK-2 instrument and the PZZ instrument.

The oil oxidation conditions in these two methods differ greatly with temperature, time of test, intensity of mixing, the presence of a catalyzer, and the amount of air supplied. Therefore, the speed and extent of the oxidation and the oxidizing polymerization of oil should also differ greatly.

The tests in the DK-2 method were made at 140°C for 25 hours and with an 0.02% catalyzer, copper naphthenate.

The tests in the PZZ method were made for two hours at 150°C for oils without additives and at 200°C for oils with additives; velocity of oil circulation, 125 liters per hour and amount of air supplied, 50 liters per hour.

The comparative results for various oils with and without additives (Table 1) show that the methods considered differ considerably not only in the absolute values of the evaluated corrosion, but also in the evaluation of the various oils.

Thus, for the majority of oils there is observed a considerably greater unit loss in the weight of the lead plates under DK-2 conditions than under PZZ conditions. Only two oils are exceptions and they contain antioxidizing DF-11 additive for which both methods give a similar evaluation. It may be seen from Table 1 that on the DK-2 instrument, oils without additives are evaluated about the same as the majority of oils with additives, except that the presence of the DF-11 additive reduces sharply the corrosive qualities of oils.

In the PZZ instrument, on the contrary, oils without additives are considerably more corrosive than oils with; oils with DF-11 differ little from oils with other additives.

To clarify the possible causes of the variations uncovered in evaluating oil by the DK-2 and PZZ methods, changes in other quality indicators of oils occurring in their process of oxidation in the DK-2 and PZZ were investigated. For this purpose, samples of oil after oxidation were analyzed for the following: kinematic viscosity at 100°C, accumulation of oxidation products (total content of impurities) and the hydrogen indicator.

Table 2 shows the results of investigations of four samples of oils. In order to obtain more reliable results, each indicator is the average of not less than four independent tests.

The data in Table 2 indicates that along with the large spread in the evaluation of the corrosion qualities of the oils by the DK-2 and PZZ methods, there are also considerable differences in the extent of oil oxidation.

As an example, we will consider AS-8 oil with the 3.5% VNII NP-360 additive. The corrosion for this oils was 115 grams per square meter in the DK-2 instrument and 0.3 grams per square meter in the PZZ. The oxidation process in the PZZ, as shown by the data, occurs more intensively than in the DK-2 instrument. Thus, for oxidation in the PZZ, the kinematic viscosity increases 2.1 centistokes, the content of contaminants (oxidation products) increases to 1.0%, and the hydrogen indicator decreases by 5.4 units. The oxidation of the same oil in the DK-2 instrument increases the viscosity only 0.06 centistokes, the content of contaminants increases 0.23%, and the hydrogen indicator decreases by 2.5 units.

Table 1

① Результаты оценки антикоррозионных свойств масел

№	② Масла с присадками	④ Коррозионность, г/м² по методу ДК-2 ⑤	по методу ПЗЗ ⑥
1	⑦ Масло АС-6 бакинское с присадкой 5% АзНИИ-8у	131	1,35
2	⑧ Масло АС-6 бакинское с присадкой 2,6% БФК, 1,4% СБ-3, 1,2% ИНХП-21	136	1,6
3	⑨ Масло АС-6 восточное с присадкой 3% СК-11, 1,2% ДФ-11	1,1	0,2
4	⑩ Масло АС-6 восточное с присадкой 3,5% АСК, 1,2% ДФ-11	2,8	3,0
5	⑪ Масло АС-8 восточное с присадкой 3,5% ВНИИ НП-360	115	0,3
6	⑫ Масло ДС-8 восточное без присадки	165	58,7
7	⑬ » АК-10 бакинское » »	162	38,5
8	» АС-10 » с присадкой 5% АзНИИ-8у	370	22,0
9	⑭ Масло АС-10 восточное с присадкой 3,5% ВНИИ НП-360	153,9	0
10	⑮ Масло АС-9,5 восточное с присадкой НП-22К	226	10,0

Translator's Note: AzNII [Azerbaydzhan Scientific Research Petroleum Institute imeni V. V. Kuybyshev].
INKhP [Institute of Petrochemical Processes]
VNII NP [All-Union Scientific Research Institute of the Petroleum Industry].

Key: 1 -- Results of evaluation of anticorrosion qualities of oils; 2 -- number; 3 -- oils with additives; 4 -- corrosion, grams per square meter; 5 -- DK-2 methods; 6 -- PZZ method; 7 -- AS-6 Baku oil with 5% AzNII-8u additive; 8 -- AS-6 Baku with 2.6% BFK, 1.4% SB-3 and 1.2% INKhP-21 additive; 9 -- AS-6 Eastern oil with 3% SK-11, 1.2% DF-11 additive; 10 -- AS-6 Eastern oil with 3.5% ASK, 1.2% DF-11 additive; 11 -- AS-8 Eastern oil with 3.5% VNII NP-360 additive; 12 -- DS-8 Eastern oil without additive; 13 -- AK-10 Baku oil without additive; 14 -- AS-10 Baku oil with 5% AzNII-8u additive; 15 -- AS-10 Eastern oil with 3.5% VNII NP-360 additive; 16 -- AS-9.5 Eastern oil with IP-22K additive.

The same difference in the nature of the change in the quality indicators of the oil when oxidized in the DK-2 and PZZ instruments is observed also for other samples of oils. Thus, the extent of oxidation of the AS-6 oil with 5% AzNII-8u additive is shown in the PZZ instrument by an increase in viscosity of 2.8 centistokes, an increase in total contaminants of 2.2%, and a decrease in the hydrogen indicator by 5 units, while in the DK-2 these are 0.18 centistokes, 0.174% and 1.9 units respectively.

Table 2

① Изменение показателей масел после окисления в приборах ДК-2 и П33

② № п.п.	③ Образцы масел	④ Метод испытания	⑤ Величина коррозии, г/м²	⑥ Кинематическая вязкость при 100 °С, сст: ⑨ до окисления	⑩ после окисления	⑪ прирост вязкости	⑦ Содержание примесей, %: ⑭ до окисления	⑯ после окисления	⑰ увеличение количества примесей	⑧ Водородный показатель pH: ⑮ до окисления	⑯ после окисления	⑫ снижение pH
⑬ 1	Масло АС-8 восточное с 3,5% ВНИИ НП-360	ДК-2	115	8,6	8,9	0,6	0,560	0,785	0,225	9,8	7,34	2,46
		П33	6,3	8,3	10,4	2,1	0,560	1,482	0,922	9,8	4,54	5,36
⑭ 2	Масло АС-6 бакинское с 2,6% БФК + 1,4% СБ-3 + 1,2% ИНХП-21	ДК-2	136	7,1	7,26	0,16	0,490	0,695	0,205	8,9	7,85	1,09
		П33	1,6	7,1	9,2	2,1	0,490	3,291	2,801	8,9	3,36	5,54
⑮ 3	Масло АС-6 восточное с 3% СК-11 + 1,2% ДФ-11	ДК-2	1,1	6,9	7,15	0,25	0,484	0,550	0,066	7,1	6,25	0,85
		П33	0,2	6,9	8,1	1,2	0,484	1,097	0,613	7,1	4,5	2,6
⑯ 4	Масло АС-6 бакинское с 5% АзНИИ-8у	ДК-2	1,31	7,1	7,29	0,18	0,556	0,730	0,174	9,45	7,55	1,90
		П33	1,35	7,1	9,9	2,8	0,556	2,733	2,177	9,45	4,38	5,07

Key: 1 -- Change in oil indicators after oxidation in the DK-2 and PZZ instruments; 2 -- number; 3 -- oil samples; 4 -- test method; 5 -- corrosion, grams per square meter; 6 -- kinematic viscosity at 100°C, centistoke; 7 -- impurity content, %; 8 -- hydrogen pH indicator; 9 -- before oxidation; 10 -- after oxidation; 11 -- increase in viscosity; 12 -- reduction in the pH; 13 -- AS-8 Eastern oil with 3.5% VNII NP-360; 14 -- AS-6 Baku oil with 2.6% BFK+1.4% SB-3+1.2% INKhP-21; 15 -- AS-6 Eastern oil with 3% SK-11+1.2% DF-11; 16 -- AS-6 Baku oil with 5% AzNII-8u; 17 -- increase in contamination; 18 -- DK-2; 19 -- PZZ.

Thus, in comparing the results of the corrosion evaluation and the analyses of oils in the DK-2 and PZZ instruments, it follows that there is a greater corrosion of the control plates with considerably less oxidation of oils in the DK-2 instrument than in the PZZ.

The suggestion may be made that the difference in the extent of oxidation may be the cause of the differences observed in the loss of the lead plates. The accumulation of a large amount of oil oxidation products in the PZZ instrument leads to the formation of tar films on the surface of the lead plates which prevent corrosion processes. The appearance of the lead plates after oil oxidation confirms this because the plates are covered with a film varying in color from yellow to brown.

The additional effect of tar films on the evaluation of the corrosion qualities of oil can be confirmed by the following data.

Table 3

(1) Результаты определения коррозии свежего и регенерированного масла АС-8 с 3,5% ВНИИ НП-360 в приборе ДК-2

(2) № п/п	(3) Образцы масел	(4) Длительность испытания, ч	(5) Величина коррозии, г/м²	(6) Кинематическая вязкость, сст: (9) до окисления	(10) после окисления	(11) прирост вязкости	(7) Содержание примесей, %: (9) до окисления	(10) после окисления	(12) увеличение примесей	(8) Водородный показатель pH: (13) свежего масла	(10) после окисления	(14) снижение
(15) 1	Масло АС-8 товарное с 3,5% присадки ВНИИ НП-360	10	0,85	8,3	8,5	0,2	0,360	0,755	0,195	9,8	7,6	2,2
		25	115		8,9	0,6		0,790	0,230		7,3	2,5
(16) 2	Масло АС-8 регенерированное с [illegible] ВНИИ НП-360	10	2,1	8,6	8,8	0,2	[illegible]	0,715	0,147	12,[illegible]	8,3	4,0?
		[illegible]	3,6?		[illegible]	0,3		[illegible]	[illegible]		[illegible]	[illegible]

Key: 1 -- Results of the determination of the corrosion of fresh and regenerated AS-8 oil with 3.5% VNII-NP-360 in the DK-2 instrument; 2 -- number; 3 -- oil samples; 4 -- length of test, hours; 5 -- amount of corrosion, grams per square meter; 6 -- kinematic viscosity, centistoke; 7 -- impurity content, %; 8 -- hydrogen pH indicator; 9 -- before oxidation; 10 -- after oxidation; 11--increase in viscosity; 13 -- fresh oil; 14 -- reduction; 15 -- AS-8 commercial oil with 3.5% VNII NP-360 additive; 16 -- AS-8 regenerated oil with 3.5% VNII NP-360.

Table 3 shows results of oxidation in the DK-2 instrument of fresh and regenerated AS-8 oil with a 3.5% VNII NP-360 additive. The corrosion of the regenerated oil was 3.6 grams per square meter and of fresh oil, 115 grams per square meter. The other oxidation indicators (changes in viscosity, contaminant content and pH) of the oils being compared varied very little. Table 3 also shows oxidation data for 10 and 25 hours for both oils. For about the same nature of oxidation, a sharp jump in corrosion was observed in the fresh oil and only a small increase in the regenerated oil. The reason for these differences is the considerable content of tar compounds in the regenerated oil which form protective films on the lead plates after several hours of oxidation.

The results of the determination of corrosion in AS-8 oil with a 3.5% VNII NP-360 additive removed from the engine of a car after operating 9,000 and 18,000 kilometers also confirm the formation of protective films of oil oxidation products.

The lead plates were found to be covered with a brown film which could not be removed by benzine and there was an increase in the weight of the plates from 0.6 to 1.2 milligrams rather than a decrease in weight.

An analysis of the results of several oil samples when oxidized in the DK-2 and PZZ instruments makes it possible to compare the corrosion qualities of oils with the change in other indicators and compare the two methods for evaluating the corrosion properties of the oils.

For the four oil samples shown in Table 2, curves were plotted on Fig. 1 for the relationships between the changes in the viscosity, increase in contaminants and the pH at the end of oxidation in each instrument, and the value of the corrosion indicator by the DK-2 and the PZZ methods. The numbers on the chart are the numbers of the oils in Table 2.

In spite of the limited test data, it is possible to note the presence of general, almost linear, relationships between the considered indicators and the value of the corrosion. In both methods, the increase in corrosion is related to the rise in viscosity and contaminants although for oxidation in the DK-2 instrument, the viscosity and the contaminants increase very little, while in the PZZ instrument they increase considerably.

The relationship between the pH and the amount of corrosion is of a different nature. In the PZZ instrument, as could be expected, oils with a smaller pH are very corrosive, while an inverse relationship is observed in the DK-2. In both diagrams, the investigated oils are located in a similar sequence. The reason for the anomalous relationship between the pH indicator and the amount of corrosion in the DK-2 instrument remains unexplained.

In Fig. 2, an attempt was made to check the correlation between similar oil indicators obtained when oxidized in both instruments. The solid line in each of the four diagrams corresponds to the full coincidence of oil indicators in both methods. With the exception of the corrosion indicator which has a scale for the DK-2 one-fifth of that for the PZZ, the scales for all other indicators are the same and the line of coincidence of the evaluations has a 45° angle. Broken lines connect test points for the corrosion indicator for ten oil samples (Table 1) and, for four samples, (see Table 2) for other indicators.

Thus, there is a nearly linear relationship in both methods for all indicators. The corrosion causes a greater loss by two-three orders of magnitude in the weight of the plates in the DK-2 method while for the other indicators (increase in viscosity, increase in contaminants and reduction in pH), the PZZ method causes greater changes approximately 7, 12 and four times respectively.

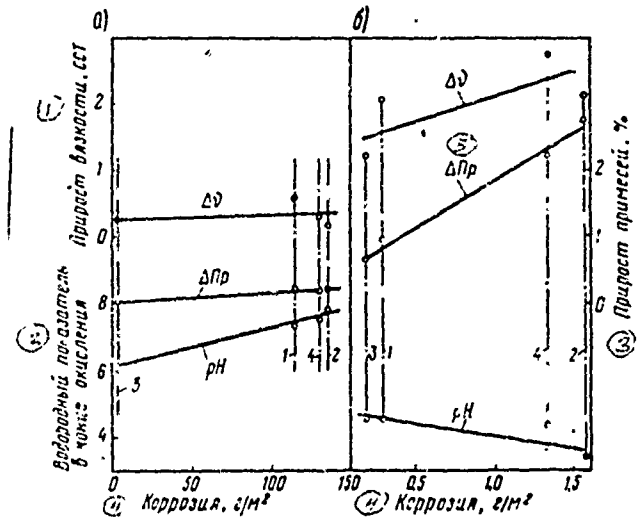


Fig. 1. Correlation curves between the corrosion indicator and the extent of oil oxidation indicator in DK-2 (a) and the PZZ (b) instruments.
Key: 1 -- increase in viscosity, centistoke; 2 -- pH after oxidation; 3 -- increase in contaminants, %; 4 -- corrosion, grams per square meter; 5 -- Δ Pr.

The comparison shows that the DK-2 method causes a more intensive corrosion of the plates but, at the same time, does not cause an essentially smaller change in the other oil oxidation indicators.

The data cited concerns oils with additives shown in Tables 1 and 2. Oils without additives have a certain anomaly which follows from the correlation diagram of the corrosion indicator where two points corresponding to these oils lie considerably below the curve for oils with additives.

The oil oxidation obtained in the two instruments makes it possible to trace the general relationship between the basic oil oxidation indicators. Fig. 3 shows the test relationship between the increase in viscosity, the increase in contaminants and the value of the pH at the end of oxidation, and between the increase in contaminants and the increase in viscosity. Each point corresponds to an average value of four independent determinations.

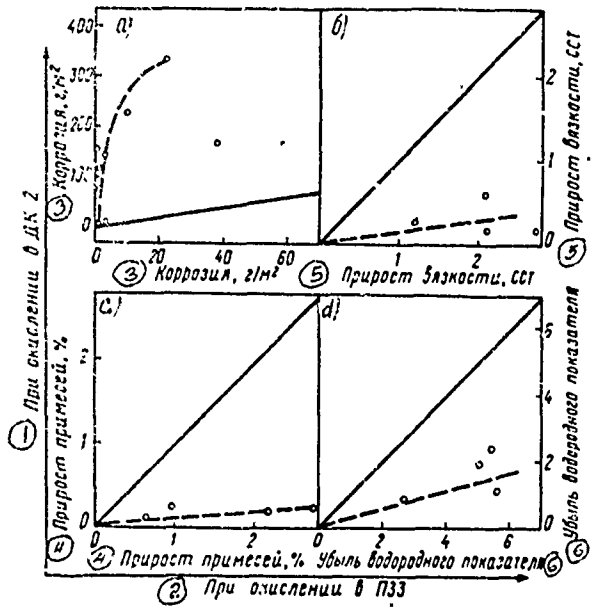
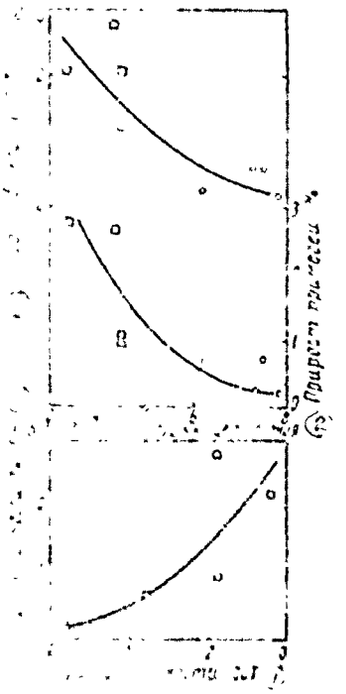


Fig. 2. Diagram of correlation between similar oil evaluation indicators when oxidized in the DK-2 and PZZ instruments: a -- corrosion; b -- change in viscosity; c -- contaminant accumulation; d -- change in pH.
Key: 1 -- oxidized in DK-2; 2 -- oxidized in PZZ; 3 -- corrosion, grams per square meter; 4 -- increase in contaminants, %; 5 -- increase in viscosity, centistokes; 6 -- decrease in the pH.

The diagrams in Fig. 3 make it possible to state that there is an essential relationship between the considered oil oxidation indicators which is independent of the type of oil and the method of oxidation. It will be possible to establish the types of these relationships when further data is accumulated.

Conclusions

On the basis of comparing the results of the determination of oil corrosion by the two methods using copper naphthenate as a catalyst in the DK-2 instrument, and the analyses of oil samples taken after the determination of corrosion in the



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film of oxidation products on the surface of the plates which prevents further corrosion of the plates.

4. The considered methods for the determination of corrosion do not give an objective evaluation of anticorrosion qualities.

5. The conclusions drawn confirm the necessity for improving the considered methods or of developing new methods for evaluating anticorrosion qualities of oils which would reflect their actual qualities exhibited under actual car engine operating conditions and making it possible to evaluate the actual operating anticorrosion qualities of oils.